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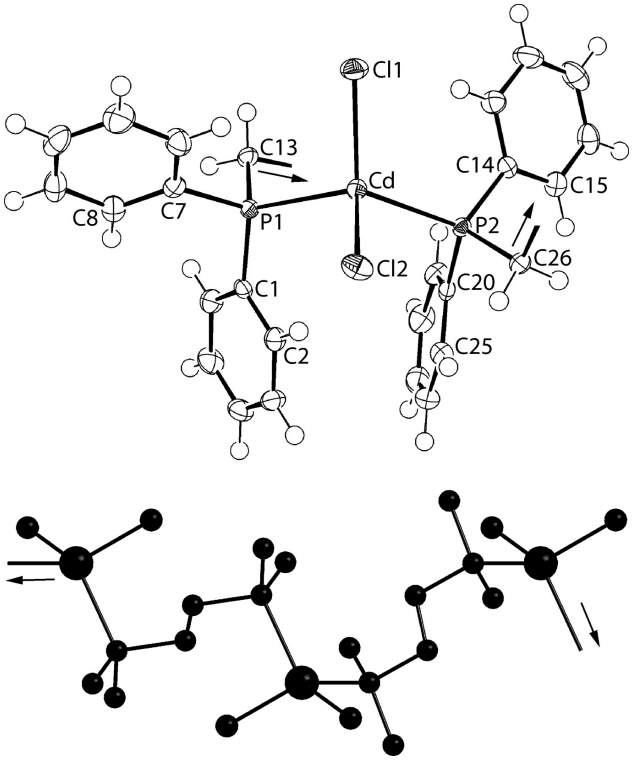
Crystal structure of *catena*-poly{[μ_2-1,2-bis(diphenylphosphino)ethane] dichloridocadmium(II)}, $C_{26}H_{24}CdCl_2P_2$



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Abstract

$C_{26}H_{24}CdCl_2P_2$, monoclinic, $P2_1/n$ (no. 14), $a = 13.2003(1)$ Å, $b = 11.4655(1)$ Å, $c = 16.7390(1)$ Å, $\beta = 100.955(1)°$, $V = 2487.25(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0173$, $wR_{ref}(F^2) = 0.0451$, $T = 100(2)$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	0.16 × 0.13 × 0.09 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	10.31 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω-scans
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	29109, 4433, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4326
$N(param)_{refined}$:	280
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Source of material

The title compound was prepared by direct crystallisation using a layering method. 1,2-Bis(diphenylphosphino)ethane (Sigma-Aldrich; 0.00597 g, 0.015 mmol) was dissolved in chloroform (Merck; 5 mL) and transferred to a 14 mL test tube. This was followed by careful layering of a buffer solution [a mixture of chloroform and ethanol (Merck; 1/1 *v*/*v*, 2 mL)]. Then, an ethanol solution (5 mL) of cadmium chloride (Acros Organic; 0.0275g, 0.015 mmol) was carefully layered upon the buffer solution. The test tube was sealed with a cap and allowed to stand under ambient conditions. Colourless blocks were formed after two days. Yield: 0.0756g (86.6%). **M. pt** (MelTemp Melting Point Apparatus): 528–531 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm^{-1}): 1401 (w) ν(P—CH_2); 1122 (m) ν(P—$C_{aromatic}$) cm^{-1}.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Crystal structure determinations of phosphane adducts of cadmium halides are relatively rare, with the chlorides,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd	0.24099(2)	0.37614(2)	0.45720(2)	0.01141(5)
Cl1	0.24002(3)	0.42277(4)	0.31518(2)	0.01976(10)
Cl2	0.14136(3)	0.21392(4)	0.49648(3)	0.01880(9)
P1	0.43166(3)	0.32444(4)	0.50754(2)	0.01034(9)
P2	0.16690(3)	0.54591(4)	0.53154(2)	0.01027(9)
C1	0.46585(13)	0.30945(14)	0.61680(10)	0.0118(3)
C2	0.38808(13)	0.27560(15)	0.65818(10)	0.0144(3)
H2	0.3208	0.2592	0.6286	0.017*
C3	0.40907(14)	0.26595(16)	0.74219(11)	0.0179(4)
H3	0.3562	0.2422	0.7701	0.021*
C4	0.50687(14)	0.29084(17)	0.78576(11)	0.0206(4)
H4	0.5210	0.2841	0.8434	0.025*
C5	0.58404(14)	0.32565(17)	0.74510(11)	0.0212(4)
H5	0.6509	0.3433	0.7750	0.025*
C6	0.56391(13)	0.33485(16)	0.66104(11)	0.0173(4)
H6	0.6171	0.3585	0.6335	0.021*
C7	0.47758(13)	0.19894(15)	0.45880(10)	0.0134(3)
C8	0.56929(14)	0.14136(16)	0.49142(12)	0.0164(4)
H8	0.6079	0.1637	0.5430	0.020*
C9	0.60379(14)	0.05108(16)	0.44790(13)	0.0212(4)
H9	0.6661	0.0115	0.4698	0.025*
C10	0.54756(16)	0.01878(17)	0.37283(12)	0.0243(4)
H10	0.5721	−0.0422	0.3431	0.029*
C11	0.45588(17)	0.07454(18)	0.34059(12)	0.0261(4)
H11	0.4171	0.0512	0.2893	0.031*
C12	0.42082(15)	0.16485(17)	0.38357(11)	0.0202(4)
H12	0.3580	0.2034	0.3616	0.024*
C13	0.51308(13)	0.44188(15)	0.48187(10)	0.0130(3)
H13A	0.5864	0.4227	0.5029	0.016*
H13B	0.5033	0.4492	0.4220	0.016*
C14	0.15531(12)	0.68822(15)	0.48320(10)	0.0119(3)
C15	0.12973(13)	0.78720(16)	0.52373(11)	0.0165(4)
H15	0.1193	0.7810	0.5782	0.020*
C16	0.11947(14)	0.89424(16)	0.48488(12)	0.0203(4)
H16	0.1023	0.9614	0.5128	0.024*
C17	0.13424(15)	0.90376(18)	0.40515(13)	0.0241(4)
H17	0.1274	0.9774	0.3787	0.029*
C18	0.15894(15)	0.80610(18)	0.36423(12)	0.0240(4)
H18	0.1688	0.8128	0.3097	0.029*
C19	0.16940(13)	0.69796(16)	0.40275(11)	0.0170(4)
H19	0.1861	0.6310	0.3745	0.020*
C20	0.23597(12)	0.56992(15)	0.63519(10)	0.0126(3)
C21	0.31405(13)	0.65336(17)	0.65099(11)	0.0165(4)
H21	0.3281	0.7011	0.6080	0.020*
C22	0.37145(14)	0.66716(18)	0.72913(12)	0.0222(4)
H22	0.4248	0.7239	0.7393	0.027*
C23	0.35093(15)	0.59816(19)	0.79242(12)	0.0229(4)
H23	0.3895	0.6082	0.8460	0.027*
C24	0.27397(14)	0.51480(18)	0.77695(11)	0.0218(4)
H24	0.2601	0.4674	0.8201	0.026*
C25	0.21690(14)	0.49968(16)	0.69913(11)	0.0173(4)
H25	0.1648	0.4415	0.6892	0.021*
C26	0.03491(12)	0.50648(15)	0.54192(10)	0.0127(3)
H26A	0.0363	0.4321	0.5721	0.015*
H26B	0.0068	0.5676	0.5734	0.015*

naturally, being the most represented. For the chlorides, the first structure determined for this class of compound was that of monomeric $CdCl_2(PPh_3)_2$ [5], featuring tetrahedrally coordinated cadmium within a Cl_2P_2 donor set. It turns out that all the other structurally determined compounds feature potentially bidentate di-phosphane ligands. Often these are chelating, leading to monomeric species such as in the case of $CdCl_2$(dppf) [6]; dppf is 1,1′-bis(diphenylphosphanyl)ferrocene. There is only a single example of bidentate, bridging di-phosphane leading to a one-dimensional coordination polymer, namely in the 1:1 structure formed between $CdCl_2$ and (R,R)-trans-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane [7]. In continuing studies into the formation of coordination polymers with cadmium(II) nodes [8–11], the crystal and molecular structures of the title one-dimensional coordination polymer $[CdCl_2(dppe)]_n$, was determined; dppe is 1,2-bis(diphenylphosphino)ethane.

The asymmetric unit is shown in the top view of the Figure (70% probability displacement ellipsoids), and comprises a cadmium(II), two chloride atoms and two half dppe molecules, each disposed about a centre of inversion [C13—C13^{i} and C26—C26^{ii} for symmetry operations (i) $1-x, 1-y, 1-z$ and (ii) $-x, 1-y, 1-z$]. The cadmium is tetrahedrally coordinated within a Cl_2P_2 donor set. The Cd—Cl1, Cl2 bond lengths of 2.4342(4) and 2.4391(4) Å are very close to each other but, there is a greater disparity in the Cd—P1, P2 bond lengths, that is, 2.5672(4) and 2.5993(4) Å, respectively. The tetrahedral angles span a range of about 20° with the most acute angle of 99.835(14)° being subtended by the Cl2 and P2 atoms. The widest angle of 121.849(15)° is subtended by the chloride atoms. As the dppe ligands are μ_2-bridging, the result is the formation of a one-dimensional coordination polymer, as shown in the lower view of the Figure (only ipso-carbon atoms are shown and all hydrogen atoms have been omitted). The chains extends along the *a*-axis direction with repeat units propagated by inversion symmetry so the topology of the chain is zig-zag.

In the crystal, the chains are connected into a three-dimensional architecture by π—π interactions occurring between centrosymmetrically-related (C7—C12) rings [inter-centroid separation = 3.8158(11) Å for symmetry operation (iii) $1-x, -y, 1-z$] as well as phenyl-C—H···π(phenyl) interactions [C3—H3···Cg(C20—C25) = 2.74 Å, C3···Cg(C20—C25) = 3.581(2) Å and angle at H3 = 148° for symmetry operation (iv) $1/2-x, -1/2+y, 3/2-z$]. In order to analyse the molecular packing in more detail, an analysis of the calculated Hirshfeld surfaces was conducted using Crystal Explorer 17 [12] following established procedures [13]. The association between

chains are dominated by non-directional H···H (50.0%) and Cl···H/H···Cl (16.4%) contacts. The presence of C···H/H···C (27.5%) along with C···C (2.5%) contacts also make discernable contributions to the surface.

Among the cadmium dihalides having a P_2CdX_2 core, the most closely related structure is that of the CdI_2(dppe) species, isolated as a di-hydrate [14]. This is also a one-dimensional coordination polymer resembling the structure reported herein.

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